Solid-state hydrolysis of cellulose and methyl α- and β-d-glucopyranosides in presence of magnesium chloride

AUTHOR(S):

Shimada, Naoki; Kawamoto, Haruo; Saka, Shiro

CITATION:

Shimada, Naoki ...[et al]. Solid-state hydrolysis of cellulose and methyl α- and β-d-glucopyranosides in presence of magnesium chloride. Carbohydrate Research 2007, 342(10): 1373-1377

ISSUE DATE:

2007-07-23

URL:

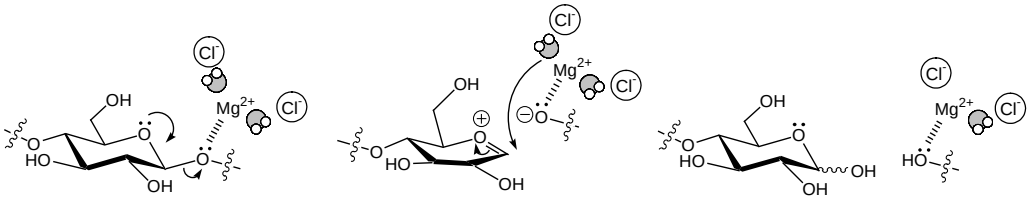
http://hdl.handle.net/2433/240767

Graphical abstract:

Solid-state hydrolysis of cellulose or methyl glucoside in presence of magnesium chloride

Naoki Shimada, Haruo Kawamoto* and Shiro Saka

Solid-state hydrolysis proceeded in cellulose or methyl glucoside in presence of hydrated magnesium chloride. This reaction was effective even at > 100 °C since the hydrated water, which is held in magnesium chloride up to > 200 °C, is used as a nucleophile.



Title:

Solid-state hydrolysis of cellulose or methyl glucoside in presence of magnesium chloride

Authors and affiliation:

Naoki Shimada, Haruo Kawamoto*, Shiro Saka

* Corresponding author: Tal/ Fax: +81-75-753-4737
Email address: kawamoto@energy.kyoto-u.ac.jp (H. Kawamoto)

Full postal address of the person to whom proofs are to be sent:
Graduate School of Energy Science, Kyoto University
Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Abstract:

Solid-state hydrolysis proceeded in cellulose or methyl glucoside in presence of hydrated magnesium chloride. This reaction was effective even at > 100 °C since the hydrated water, which is held by $MgCl_2$ up to > 200 °C, is utilized as a nucleophile. Excess water made this reaction ineffective due to the competition between water and glycosidic oxygen in coordinating with Mg^{2+}, a Lewis acid. Consequently, this hydrolysis reaction is characteristic of solid-state.

Keywords:

Cellulose; Magnesium chloride; Hydrolysis; Solid-state hydrolysis; Methyl glucoside; Lewis acid.

Text:

Interactions between carbohydrates and alkaline earth metal halides are important in their thermochemical reactions[1-4] as well as their biological roles. Many studies relating to the latter topics deal with the interactions in solid-state[5-9] and aqueous solution[10-12] to understand the biological processes such as calcium storage,[13] calcification,[14] calcium-dependent cell-cell adhesion[15, 16] and DNA-stabilization.[17] Alkaline earth metal halide also affects the carbohydrate pyrolysis.[1-4] Increasing yields of char, carbon monoxide and water and decreasing yield of levoglucosan (1,6-anhydro-β-D-glucopyranoside) have been reported as the major influences on cellulose pyrolysis.[1-4] Our previous study[4] has shown that alkaline earth metal chlorides ($MgCl_2$, $CaCl_2$) reduced the pyrolysis-temperature of cellulose substantially. This communication deals with the solid-state reaction of cellulose or methyl glucoside in the presence of $MgCl_2$ to identify the activation mechanism of cellulose pyrolysis.

Cellulose sample containing $MgCl_2$ (0.5 mol/mol of the glucose-unit of cellulose) was heated in air (1 atm) at 105 ^oC for 24 h. The resulting cellulose sample is shown in Fig. 1 with the X-ray diffraction (XRD) pattern. Although light-brown color of the sample indicates some reaction occurring during the heat treatment, the XRD pattern shows the native cellulose I-type of crystal structure remained. From the analysis of the methanol extract of the sample, small amount of 5-hydroxymethyl furfural (5-HMF) was identified.

Figure 2 summarizes the gel-peameation chromatograms (GPC) obtained for the cellulose samples (in air/105 ^oC/1-24 h) after conversion into the phenylcarbamate derivatives. Degree of polymerization (DP) of cellulose decreases from 700 to 400

(polystyrene standard) up to the 12 h-treatment. The peak corresponding to DP 60 is also observed along with the peak (DP 400) for the 24 h-treated sample. Thus, the DP of cellulose is reduced stepwise in the presence of $MgCl_2$ from 700 to 400 and then 60. This DP reduction would relate to the leveling-off DP of cellulose. In the heterogeneous (suspension) hydrolysis of native cellulose (cellulose I) with inorganic acids such as sulfuric acid, the DP decreases up to the leveling-off DP of 200-300.[18-21] Similar leveling-off DP has been reported under pyrolysis conditions.[22-24] As for regenerated cellulose (cellulose II) such as viscose rayon, some smaller leveling-off DP around 30-100 has been reported in acid hydrolysis.[18, 19, 21] Although the details of the mechanism are not known presently, the leveling-off DPs of 400 and 60 are close to those of cellulose I and II, respectively. This DP-reduction was substantially inhibited with excess amount of water (Fig. 2).

Reduction of DP and 5-HMF formation indicate the $MgCl_2$ acting as a Lewis acid in transglycosilation and dehydration reactions, respectively. To investigate these reactions further, model experiments with methyl α- and β-D-glucosides were conducted under the similar conditions. Figure 3 shows the XRD patterns of the glucoside-$MgCl_2 \cdot 2H_2O$ mixture at various ratios, which were obtained by grinding these two solid substances in mortar. Relative peak intensities drastically changed with increasing amount of $MgCl_2 \cdot 2H_2O$. For methyl α-D-glucoside, intensities of two large peaks at $2\theta = 10^o$ and 15^o substantially decrease with 0.5 mol equivalent of $MgCl_2 \cdot 2H_2O$, and the XRD pattern changes further with increasing the $MgCl_2 \cdot 2H_2O$ addition level [main peaks: $2\theta = 27^o$ and 41^o (1.0 mol equivalent), $2\theta = 33^o$ (5.0 mol equivalent)]. Similarly decrease in the small angle ($2\theta = 11^o$) peak-intensity is observed also in the methyl β-D-glucoside-$MgCl_2 \cdot 2H_2O$ mixture. Since any

transformation of methyl α- and β-D-glucosides was not detected without heat treatment, these changes in the XRD patterns would be derived from some glucosides-$MgCl_2$ interactions in solid state. Change in the crystal structures of these glucosides was not studied further.

In heating the methyl β-D-glucoside-$MgCl_2 \cdot 2H_2O$ mixture (1 : 0.5, mol/mol) in air (1atm) at 105 °C for 4 h, glucose was obtained in a 21.5% yield, which corresponds to about 70% of the reacted glucoside. Influence of water on this solid-state hydrolysis was also studied for methyl α- and β-D-glucosides. As shown in Fig. 4, maximum reactivities were obtained at the water levels (mol/mol of $MgCl_2$) of 6 (β-glucoside) and 2 (α-glucoside), respectively. Reduced reactivity at higher water-level indicates that this hydrolysis is characteristic of solid-state and not effective in water. Competition between water and glycosidic oxygen in coordinating with Mg^{2+} is considered as a reason. Low reactivity at the lower water-level could be explained with the back reaction in transformation into the oxonium ion. Without a nucleophile, the oxonium ion could be converted to the glucoside again by attacking of methoxide anion from the same direction due to the other side blocked in the crystals.

Based on the present results, a unique solid-state hydrolysis mechanism is proposed with utilizing the hydrated water as a nucleophile (Scheme 1). It is well-known that the hydrated $MgCl_2$ ($MgCl_2 \cdot xH_2O$) has the structure of hydrated Mg^{2+} surrounded by Cl anion.[25, 26] The water is also reported to be exchangeable with some electron donors (Lewis bases) such as methanol[27] and ethanol.[28, 29] These lines of information indicate that the Mg^{2+} in $MgCl_2 \cdot xH_2O$ would be able to coordinate with the oxygen atoms including the glycosidic oxygen as a Lewis acid, and the latter coordination catalyzes the glycosidic bond cleavage. This is also supported with the

strong solid-solid interactions indicated by the change in the XRD patterns (Fig. 3). Coordination of the Mg^{2+} to the sucrose oxygen atoms in their concentrated aqueous solution has also been indicated from the IR and ^{13}C-NMR spectra.[12] Although the addition of NaCl or KCl weakened the H-bond network between sucrose and water, the possible interaction between Mg^{2+} and the oxygen atoms of sucrose has been indicated by the addition of $MgCl_2$. With calcium chloride, similar hydrolysis reaction was also observed. Thus, such reaction would be effective with various alkaline earth metal halides.

Hydrolysis reaction proceeding in open reactor even at the higher temperature than the boiling point of water is a characteristic feature of this solid-state hydrolysis. The hydrated water is not easily removed even at such high temperature as shown in the dehydration behaviors (Fig. 5) of the hydrated $MgCl_2$ and $CaCl_2$ samples, which were prepared by drying their aqueous solutions (105 ^{o}C for 24 h) after evaporation *in vacuo*.

During pyrolysis of cellulose impregnated with alkaline earth metal chloride, such solid-state hydrolysis would proceed to form smaller fragments with reducing end-groups, and this would relate to the activation mechanism of cellulose pyrolysis. The present findings also would give useful information to oligosaccharide production, saccharification of cellulose, polysaccharide stability and so on.

1. Experimental

1.1 Materials

Filter paper (Kiriyama No. 704, oven dried at 105 ^{o}C for 24 h) was used as a cellulose sample. Aqueous solution (125 μL) of $MgCl_2$ (0.76 mol L^{-1}) was added to

the filter paper (30 mg) dropwise. This amount of solution was completely absorbed in the filter paper. The resulting paper was dried in an oven (105 °C) for 24 h. The amount of $MgCl_2$ corresponds to 0.5 mol/mol of the glucose-unit of cellulose.

Methyl α- and β-D-glucosides (Nacalai Tesque Co.) were used after drying in an oven (105 °C) for 24 h. Hydrated water in methyl β-D-glucoside was completely removed under these conditions. $MgCl_2 \cdot 6H_2O$ was purchased from Sigma-Aldrich Japan K.K. $MgCl_2 \cdot 0.75H_2O$ was obtained from Nacalai Tesque Co. as dehydrated magnesium chloride. Other hydrated magnesium chloride samples ($MgCl_2 \cdot xH_2O$) (x = 2, 10 and 20) were prepared from $MgCl_2 \cdot 6H_2O$ as follows. $MgCl_2 \cdot 2H_2O$ was prepared by drying $MgCl_2 \cdot 6H_2O$ in an oven (105 °C) for 24 h. $MgCl_2 \cdot 10H_2O$ and $MgCl_2 \cdot 20H_2O$ were prepared by adding proper amount of water to $MgCl_2 \cdot 6H_2O$. Hydrated water contents of these samples were measured by thermogravimetry with Shimadzu TGA-50 [temperature program: room temperature to 750 °C (10 °C min^{-1}) under N_2-flow (50 mL min^{-1})]. Methyl α- or β-D-glucoside-$MgCl_2 \cdot xH_2O$ mixture was prepared by grinding in a mortar for 20 s under dry nitrogen-flow and stored in a sealed vial.

1.2 Reaction and product analysis

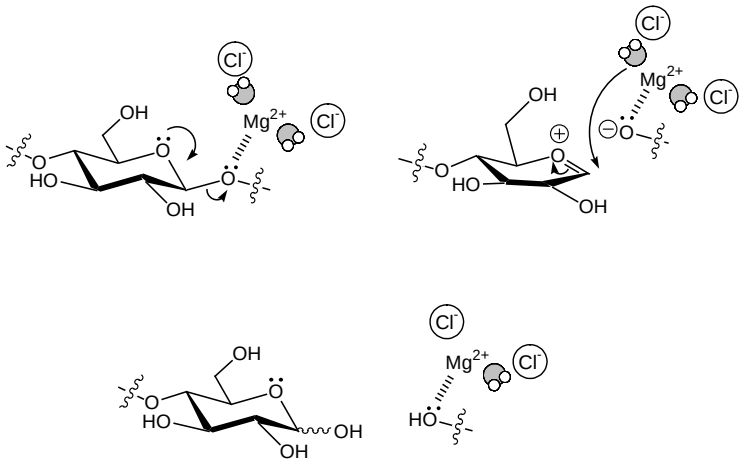
Cellulose sample impregnated with $MgCl_2$ or methyl α- or β-D-glucoside (30 mg)-$MgCl_2 \cdot xH_2O$ (x = 0.75, 2 or 6) mixture (1: 0.5 mol/mol) was taken in an open vial and heated in an oven (105 °C) for adequate reaction time. Reaction of the mixture with $MgCl_2 \cdot xH_2O$ (x = 10 or 20) was conducted in a closed ampoule to prevent the evaporation of water.

Glucose and unreacted glucoside were quantified with the ^{1}H-NMR spectrum of the reaction mixture extracted with D_2O (1mL) containing 2-furoic acid as an internal standard. ^{1}H-NMR spectra were measured with a Bruker AC-400 (400MHz) spectrometer. XRD patterns of the samples were recorded with a Rigaku RINT 2000V (Cu Kα, λ = 1.542Å, 40 kV, 30 mA). DP of cellulose sample was evaluated with GPC (polystyrene standard) after conversion into the phenylcarbamate derivative according to the literature.[30] Phenyl isocyanate (0.33 mL) and pyridine (1.0 mL) was added to the cellulose sample and vigorously stirred at 80 ºC for 48 h. After the reaction, MeOH (2.0 mL) was added to the reaction mixture to quench the reaction, and then, the resulting solution was evaporated *in vacuo* and dried over P_2O_5 in a vacuum desiccator for 24 h. The obtained mixture was redissolved in THF and analyzed with GPC [Shimadzu LC-10A, column: Shodex KF803L + KF806, eluent: THF, flow rate: 0.6 mL min^{-1}, detector: UV 254 nm, column temperature: 40 ºC].

References:

1 Tsuchiya, Y., Sumi, K. *J. Appl. Polymer Sci.* **1970**, *14*, 2003-2013.
2 Kawamoto, H., Yamamoto, D., Saka, S., unpublished data.
3 McGrath, T. E., Hoffman, J. A., Wooten, J. B., Hajaligol, M. R. *Prep. Symp. – Am. Chem. Soc. Div. Fuel Chem.* **2002**, *47*, 418--419.
4 Shimada, N., Kawamoto, H., Saka, S., unpublished data.
5 Terzis, A. *Cryst. Struc. Commun.* **1978**, *7*, 95-99.
6 Tajmir-Riahi, H. A. *Carbohydr. Res.* **1983**, *122*, 241-248.
7 Dheu-Andries, M. L., Pérez, S. *Carbohydr. Res.* **1983**, *124*, 324-332.
8 Tajmir-Riahi, H. A. *J. Inorg. Biochem.* **1984**, *22*, 55-64.
9 Tajmir-Riahi, H. A. *Carbohydr. Res.* **1984**, *127*, 1-8.
10 Carper, W. R., Coffin, D. B., Addis, J. R. *Spectrochim. Acta* **1989**, *45A*, 391-392.
11 Bailey, G. D., Carper, W. R. *J. Inor. Biochem.* **1993**, *52*, 99-108.
12 Rondeau, P, Sers, S., Jhurry, D., Cadet, F. *Appl. Spectrosc.* **2003**, *57*, 466-472.

13 Farber, S. J., Schubert, M., Schuster, N. *J. Clin. Invest.* **1957**, *36*, 1715-1722.
14 Bowness, J. M. *Clin. Orthop. Rel. Res.* **1968**, *59*, 233-247.
15 Turner, R. S., Burger, M. M. *Nature* **1973**, *244*, 509.
16 Pessac, B., Defendi, V. *Science* **1972**, *175*, 898-900.
17 Eichhorn, G. L. *Nature* **1962**, *194*, 474-475.
18 Battista, O. A., Coppick, S. *Text. Res. J.* **1947**, *17*, 419-422.
19 Mehta, P. C., Pacsu, E. *Text. Res. J.* **1948**, *18*, 387-395.
20 Battista, O. A., Coppick, S., Howsmon, J. A., Morehead, F. F., Sisson, W. A. *J. Ind. Eng. Chem.* **1956**, *48*, 333-335.
21 Sharples, A. *Trans. Faraday Soc.* **1958**, *54*, 913-917.
22 Golova, O. P., Krylova, R. G. *Dokl. Akad. Nauk., SSSR* **1957**, *116*, 419.
23 Halpern, Y., Patai, S. *Isr. J. Chem.* **1969**, *7*, 673-683.
24 Broido, A., Javier-Son, A. C., Ouano, A. C., Barral, E. M. *J. Appl. Polym. Sci.* **1973**, *17*, 3627-3635.
25 Angell, C. A., Gruen, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 5192-5198.
26 Marques, M. A., Marques, M. I. de B. *Proc. Kon. Ned. Akad. Wet.* **1974**, *B77*, 286-302.
27 Halut-Desportes, S., Philoche-Levisalles, M. *Acta Crystallogr.* **1978**, *B34*, 432-435.
28 Valle, G., Baruzzi, G., Paganetto, G., Depaoli, G., Zannetti, R., Marigo, A. *Inorg. Chim. Acta* **1989**, *156*, 157-158.
29 Bart, J. C. J., Roovers, W. *J. Mater. Sci.* **1995**, *30*, 2809-2820.
30 Isogai, A., Usuda, M. *Mokkuzai Gakkaisahi* **1991**, *37*, 339-344.



Scheme 1. A solid state hydrolysis mechanism proposed for the mixture of cellulose with hydrated $MgCl_2$.

Figures:

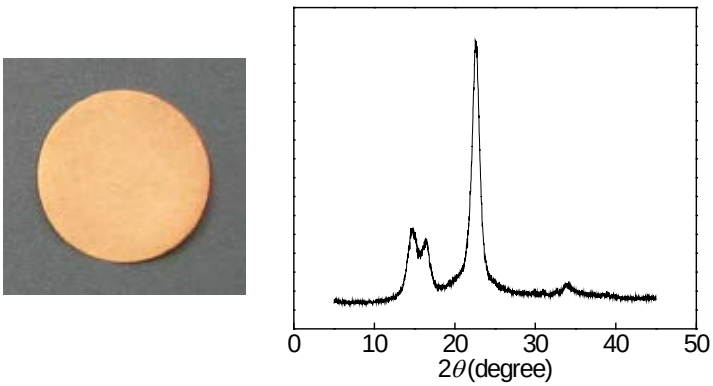


Figure 1. The cellulose sample ($MgCl_2$ content: 0.50 mol/mol of the glucose-unit in cellulose) after heat treatment in air (1 atom) at 105 ^{o}C for 24 h with the XRD pattern.

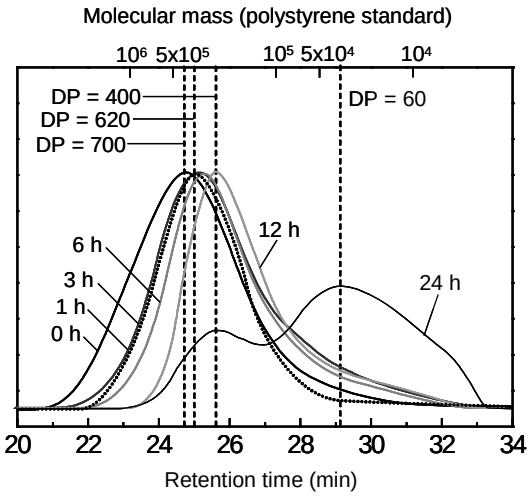


Figure 2. GPC chromatograms of the cellulose samples ($MgCl_2$ content: 0.50 mol/mol of the glucose-unit in cellulose, phenyl carbamate derivates) after heat treatment in air (1 atm) at 105 °C for 1-24 h: ..... : 24 h heating in the presence of water (0.5 mL/30 mg of cellulose) (in an closed ampoule).

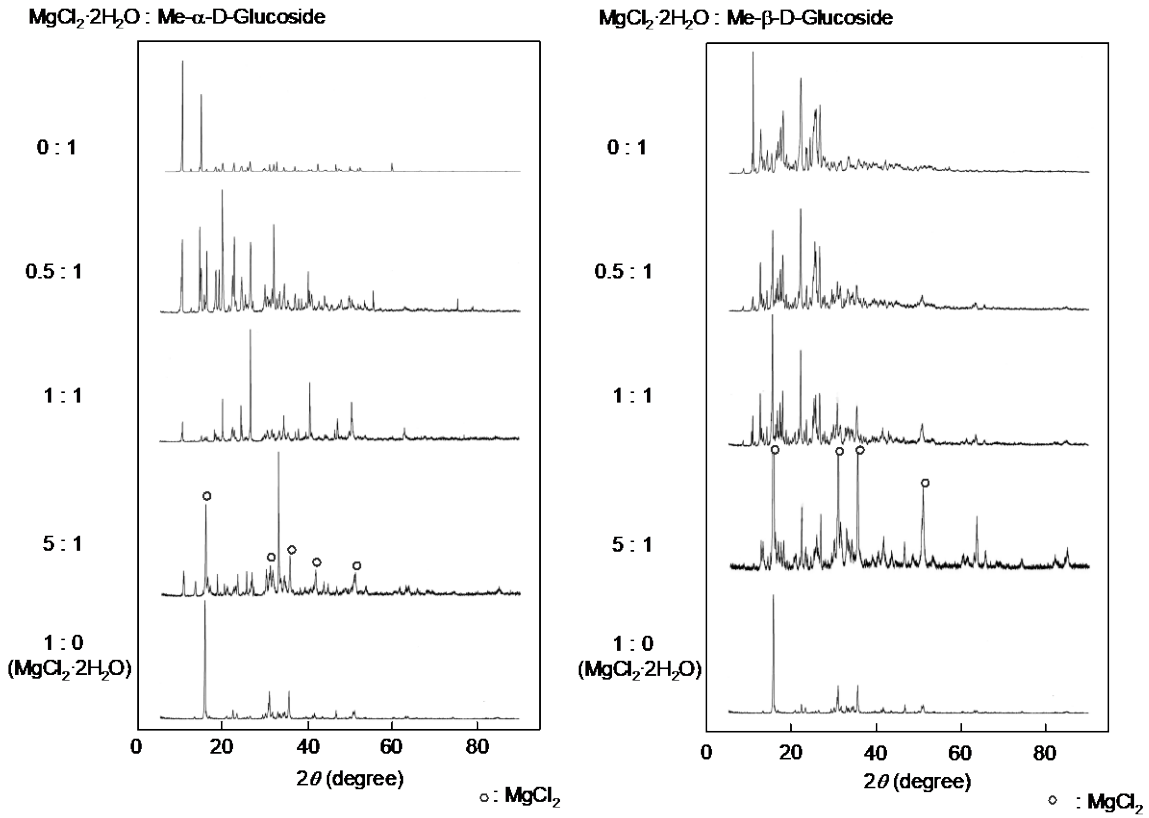


Figure 3. Change in the XRD patterns of methyl α- and β-D-glucosides mixed with increasing amount of $MgCl_2 \cdot 2H_2O$.

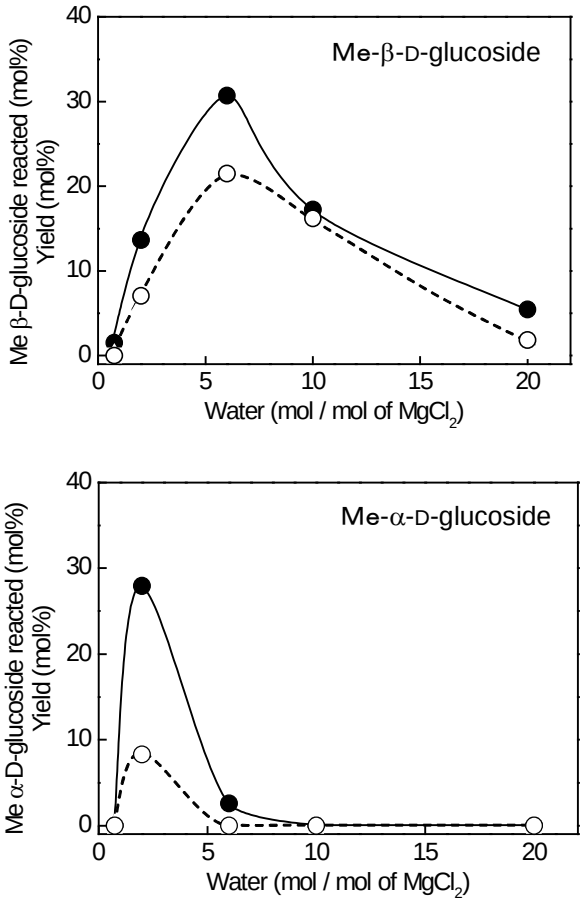


Figure 4. Reactivity and the product yields in heat-treatment of methyl α- or β-D-glucoside mixed with $MgCl_2$ (0.50 mol/mol of glucoside) in air (1 atm) at 105 °C for 4 h: (●) glucoside reacted, (○) glucose yield.

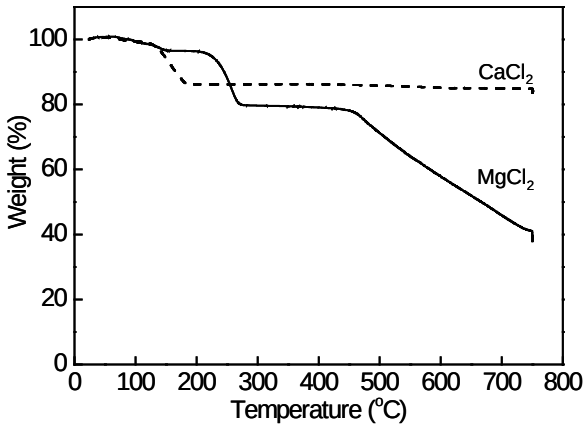


Figure 5. TG curves of the $MgCl_2$ and $CaCl_2$ samples (without any sugar components) obtained by drying their aqueous solutions at 105 °C for 24 h after evaporation *in vacuo*: TG conditions: room temperature to 750 °C (10 °C min^{-1}) under N_2-flow (50 mL min^{-1}).